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Description	Field of the invention	This invention relates to detergent compositions that clean well and also act as textile softeners.	Background of the invention	Numerous attempts have been made to formulate laundry detergent compositions that have both good cleaning properties and also textile softening properties so as to avoid the need to use a separate rinse-added textile softener product in addition to the usual laundry detergent. As cleaning by definition involves the removal of material from the textile surface and as textile softening normally involves deposition of material onto the same surface, these attempts have necessarily required a compromise in formulation to be reached between cleaning and softening performance.	Furthermore, the most common commercially available organic textile softening compounds are cationic materials that are reactive towards the anionic surfactants used in conventional laundry detergents. If both types of material are formulated in a single product, they tend to interact on addition to a wash liquor and, although in some instances the resulting complex has useful textile softening properties, its formation normally depresses the cleaning performance of the formulation and is therefore generally considered undesirable.	In order to overcome this problem, compositions have been proposed that have sought to minimise the mutual reactivity of the anionic and cationic materials by the addition of compatibilising compounds such as the amido amines and fatty acids described in U.S. Patent Nos. 3,886,075 and 3,954,632. An alternative approach has been to incorporate one of the reactant materials in a form that inhibits its contact with the other in the wash liquor and examples of this type of formulation are taught in U.S. Patent Nos. 3,936,537 and 3,644,203. The performance of these compositions is however sensitive to the washing conditions that are employed.	In an attempt to avoid the reactivity problem altogether, nonionic surfactants have been proposed in place of the conventional anionic surfactants and compositions of this type are described in e.g. British Patent Specification No. 1,079,388, German Auslegeschrift 1,220,956 and U.S. Patent No. 3,607,763. However it has been found that levels of nonionic surfactant sufficient to provide good cleaning impair the softening of the cationic softener. Another proposal to provide acceptable cleaning and textile softening by avoiding the surfactant-softener interaction has been made in British Patent Specification No. 1,514,276 which teaches the use of certain long chain tertiary amines that are nonionic in character at the wash liquor pH existing when a conventional laundry detergent is used. European Patent Application Publication Nos. 0011340 and 0023367 also disclose cleaning and softening compositions comprising a tertiary amine, containing at least one and preferably two C ₁₀ -C ₂₆ alkyl groups and being of nonionic character under alkaline conditions, in combination with a smectite-type clay in an alkaline anionic surfactant-based detergent. The use of smectite-type clays as softening agents is detergent compositions is taught in British Patent Specification No. 1,400,898. This type of softening agent does not affect the cleaning performance of the detergent composition but, if used on its own, requires a high level of incorporation for effective softening performance possibly because the deposition of the clay on fabrics is not very efficient in the presence of anionic surfactants.	It has now been found that detergent compositions containing smectite-type clays and certain cationic compounds can be formulated which have cleaning performance equivalent to that of commercially available heavy duty laundry detergents together with textile softening performance that approaches that of rinse added fabric softeners.	Summary of the invention	According to the present invention there is provided a granular detergent composition comprising, by weight of the composition, (a) 5-10% of an anionic surfactant from water soluble salts of alkyl benzene sulfonates, alkyl sulfates, para- (b) from 2% to 12% of an impalpable smectite-type clay mineral of particle size less than 50 µm having an ion exchange capacity of at least 50 meq per 100g selected from sodium and calcium montmorillonite, sodium hectorite and sodium saponite; (c) from 10% to 80% of a detergent builder salt; and (d) optionally other laundry detergent components characterised in that the composition also comprises; (e) 1-3% of a water soluble nitrogenous cationic organic compound selected from quaternary ammonium
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compounds of formula $R_7R_8R_9R_{10}N^+X^-$ wherein R_7 is C_8 - C_{14} alkyl, each of R_8 , R_9 and R_{10} is independently C_1 - C_4 alkyl or hydroxyethyl and X is an anion, said cationic compound being present as a solid component dry mixed with spray dried granular components of said composition or as a spray-on of a solution or dispersion to the surface of, or as part of spray dried granules comprising components (a) (c) and optionally (b) and/or (d); provided that the molar ratio of component (e) to (a) is less than 1:1; the amounts of (a), (b), (c), (e), and, if present, (d) comprising a total of 100%, the optional components (d) being comprised by nanionic and zwitterionic surfactants, bleaching agents and organic precursors therefor, suds suppression agents said suspending and anti redeposition agents, enzymes optical brighteners, colouring agents and perfumes.

Preferably component (e) is a C_{12} - C_{14} alkyl tri C_1 - C_4 alkyl or C_1 - C_4 hydroxy alkyl ammonium salt and component (b) comprises a montmorillonite. In an especially preferred form of this embodiment component (e) is added to preformed spray dried detergent granules comprising components (a), (b) and (c).

Detailed description of the invention

In this broadest aspect the invention comprises three components, namely the anionic surfactant component (a), the water soluble cationic component (e), and the smectite type clay component (b)

The anionic surfactant

A wide range of anionic surfactants can be used in the compositions of the present invention.

Suitable anionic non-soap surfactants are water soluble salts of alkyl benzene sulfonates alkyl sulfates, paraffin sulfonates and alphaolefin sulfonates. Soaps are also suitable anionic surfactants.

Especially preferred alkyl benzene sulfonates have 9 to 15 carbon atoms in a linear or branched alkyl chain, more especially 11 to 13 carbon atoms. Suitable alkyl sulfates have 10 to 22 carbon atoms in the alkyl chain, more especially from 12 to 18 carbon atoms.

Suitable paraffin sulfonates are essentially linear and contain from 8 to 24 carbon atoms, more especially from 14 to 18 carbon atoms; Suitable alphaolefin sulfonates have 10 to 24 carbon atoms, more especially 14 to 18 carbon atoms; alphaolefin sulfonates can be made by reaction with sulfur trioxide followed by neutralization under conditions such that any sultones present are hydrolyzed to the corresponding hydroxy alkane sulfonates.

The alkyl chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium, or alkanol-ammonium cations; sodium is preferred. Mixtures of anionic surfactants are contemplated by this invention; a satisfactory mixture contains alkyl benzene sulfonate having 11 to 13 carbon atoms in the alkyl group and alkyl sulfate having 12 to 18 carbon atoms in the alkyl group.

Suitable soaps contain 8 to 18 carbon atoms, more especially 12 to 18 carbon atoms. Soaps can be made by direct saponification of natural fats and oils such as coconut oil, tallow and palm oil, or by the neutralization of free fatty acids obtained from either natural or synthetic sources. The soap cation can be alkali metal, ammonium or alkanol-ammonium; sodium is preferred.

The composition contain 5-10% of anionic surfactant.

The water-soluble anionic compound

The second component of the compositions of the present invention is an organic water soluble nitrogenous compound. This can be cationic any quaternary ammonium compound of formula.



wherein R_7 is C_8 - C_{14} alkyl, each of R_8 , R_9 , and R_{10} is independently selected from C_1 - C_4 alkyl and hydroxyethyl and X is an anion.

The preferred alkyl chain length for R_7 is C_{12} - C_{14} particularly where the alkyl groups is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohol synthesis. Preferred groups for R_8 , R_9 and R_{10} are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds are
coconut trimethyl ammonium bromide
coconut methyl dihydroxyethyl ammonium bromide
decyl triethyl ammonium chloride

decyl dimethyl hydroxyethyl ammonium bromide
myristyl trimethyl ammonium methyl sulphate

As stated previously, the compositions of the present invention combine good softening and cleaning performance and in order to maintain the latter it is essential that the overall surfactant character be anionic. The molar ratio of the cationic component (e) to the anionic surfactant component (a) should therefore be less than 1:1 and desirably should be less than 1:1.5. In preferred embodiments of the invention such as heavy duty laundry detergent formulations, the molar ratio should be less than 1:2.

Subject to these constraints the cationic compound will be present in an amount of from 1% to 3% by weight of the composition.

The smectite-type clay

The third component of the invention is a smectite-type clay having a particle size which cannot be perceived tactilely. Impalpable clays have particle sizes below 50 microns (μm); the clays used herein normally have a particle size range of from 5 microns (μm) to less than 50 microns (μm).

The clay minerals can be described as expandable, three-layer clays, i.e., aluminosilicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100 g. of clay and preferably at least 60 meq/100 g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

These are two distinct classes of smectite clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in the outer layers. The dioctahedral minerals are primarily trivalent metal ion-based clays and are comprised of the prototype pyrophyllite and the members montmorillonite $(\text{OH})_4\text{Si}_4\text{y}(\text{Al}_{4-x}\text{Mg}_x)\text{O}_{20}$, nontronite $(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Al}_{4-x}\text{Fe}_x)\text{O}_{20}$, and volchonskoite $(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Al}_{4-x}\text{Cr}_x)\text{O}_{20}$, where x has a value of from 0 to 4.0 and y has a value of from 0 to 2.0. Of these only montmorillonites having exchange capacities greater than 50 meq/100 g. are suitable for the present invention and provide fabric softening benefits.

The trioctahedral minerals are primarily divalent metal ion based and comprise the prototype talc and the members hectorite $(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Mg}_{6-x}\text{Li}_x)\text{O}_{20}$, saponite $(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Zn}_{5-x}\text{Al}_x)\text{O}_{20}$, vermiculite $(\text{OH})_4\text{Si}_{8-y}\text{Al}_y(\text{Mg}_{6-x}\text{Fe}_x)\text{O}_{20}$, wherein y has a value of 0 to 6.0. Hectorite and saponite are the only minerals in this class that are of value in the present invention, the fabric softening performance being related to the type of exchangeable cationic as well as to the exchange capacity. It is to be recognized that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure.

As noted hereinabove, the clays employed in the compositions of the present invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions, and lithium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation.

Smectite clay $(\text{Na})^+ = \text{smectite clay } (\text{NH}_4)^+ + \text{NaOH}$. Since in the foregoing equilibrium reaction one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milli-equivalents per 100 g. of clay (meq/100 g). The cation exchange capacity of clays can be measured in several ways, including by electro dialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from 2 meq/100 g. for kaolinites to 150 meq/100 g., and greater, for certain smectite clays. Illite clays although having a three layer structure, are of a non-expanding lattice type and have an ion exchange capacity somewhere in the lower portion of the range, i.e., around 26 meq/100 g. for an average illite clay. Attapulgites, another class of clay minerals, have a spicular (i.e. needle-like) crystalline form with a low cation exchange capacity (25-30 meq/100 g.). Their structure is composed of chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms.

It has been determined that illite, attapulgite, and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the present compositions. However, sodium montmorillonites, saponites, and hectorites, and calcium montmorillonites have been found to show useful fabric softening benefits when incorpo-

rated in the compositions in accordance with the present invention.

Specific non-limiting examples of such fabric softening smectite clay minerals are:

Sodium montmorillonite

Brock
Volclay BC
Gelwhite GP
Thixo-Jel
Ben-A-Gel

Sodium hectorite

Veegum F
Laponite SP

Sodium saponite

Barasym NAS 100

Calcium montmorillonite

Soft Clark
Gelwhite L
Imvite K

Accordingly, smectite clays useful herein can be characterised as montmorillonite, hectorites, and saponite clay minerals having an ion exchange capacity of at least 50 meq/100 g. and preferably at least 60 meq/100 g. Most of the smectite clays useful in the compositions herein are commercially available under various trade names, for example, Thixogel No. 1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Imvite K from Industrial Mineral Ventures; Volclay BC and Volclay 325, from American Colloid Co., Skokie Illinois; and Veegum F from R. T. Vanderbilt. It is to be recognised that such smectite minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

Within the classes of montmorillonites, hectorite and saponite clay minerals having a cation exchange capacity of at least 50 meq/100 g., certain clays are preferred for fabric softening purposes. For example, Gelwhite GP is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in detergent softening compositions. Imvite K is also very satisfactory.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14×10^{-10} x-ray diffraction pattern. This characteristic exchange pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the compositions disclosed herein.

The smectite clay minerals useful in the present invention are hydrophilic in nature, i.e., they display swelling characteristics in aqueous media.

When used in compositions according to the invention, the smectite clay is present in an amount of from 2% to 12% by weight of the composition.

The detergent builder salt

A detergent builder salt forms component (c) of the compositions of the invention and can be inorganic or organic in character. Non limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, and silicates. Specific examples of such salts include the sodium and potassium tetraborates, bicarbonates, carbonates, tri-polyphosphates, pyrophosphates, penta-polyphosphates and hexametaphosphates. Sulphates are usually also present.

Examples of suitable organic alkaline detergency builder salts are:

(1) water-soluble amino polyacetates, e.g., sodium and potassium ethylenediaminetetraacetates nitrilotriacetates, N-(2-hydroxyethyl)nitrilotriacetates and diethylene triamine pentaacetates;

(2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates;

(e) water-soluble polyphosphonates, including sodium, potassium and lithium salts of methylenediphosphonic acid and aminopolymethylene phosphonates such as ethylenediaminetetramethylenephosphonate and diethylene triaminepentamethylene phosphonate.

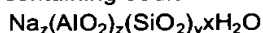
(4) water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethylsuccinic acid, 2-oxa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, mellitic acid and pyromellitic acid.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent No. 755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

Another type of detergency builder material useful in the present compositions and processes comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1,424,406.

Preferred water soluble builders are sodium tripolyphosphate and sodium silicate, and usually both are present. In particular, it is preferred that a substantial proportion, for instance, from 3% to 15% by weight of the composition of sodium silicate (solids) or ratio (weights ratio $\text{SiO}_2:\text{Na}_2\text{O}$) from 1:1 to 3.5:1 be employed.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates, particularly those described in Belgian Patent 814.874 issued November 12, 1974. This patent discloses and claims detergent compositions containing sodium aluminosilicates of the formula



wherein z and y are integers equal to at least 6, the molar ratio of z to y is in the range of from 1.0:1 to 0.5:1 and x is an integer from 15 to 264. A preferred material is $\text{Na}_{12}(\text{SiO}_2\text{AlO}_2)_{12}27\text{H}_2\text{O}$. If present, incorporation of 5% to 25% by weight of aluminosilicate is suitable, partially replacing water-soluble builder salts, provided that sufficient water-soluble alkaline salts remain to provide the specified pH of the composition in aqueous solution.

The detergency builder salts are included in amounts of from 10% to 80% by weight of the composition, preferably from 20% to 70% and most usually from 30% to 60% by weight.

The detergent compositions of the present invention may of course include, as optional ingredients, components that are usually found in laundry detergents,

These include nonionic and zwitterionic surfactants, bleaching agents and organic precursors thereof, suds suppression agents, soil suspending and anti-redeposition agents, enzymes, optical brighteners, colouring agents and perfumes.

Nonionic and zwitterionic surfactants may be incorporated in amounts of up to 50% by weight of the total surfactant but normally are present in amounts of less than 30% of the total surfactant. By 'total surfactant' is meant the sum of the anionic surfactants (a), cationic component (e) and any added nonionic and/or zwitterionic surfactant. The incorporation of 15-25% nonionic surfactant based on the total surfactant weight (corresponding to 1-2% on a total composition basis) has been found to provide advantages in the removal of oily soils. Suitable nonionics are water soluble ethoxylated materials of HLB 11.5-17.0 and include (but are not limited to) C_{10} - C_{20} primary and secondary alcohol ethoxylates and C_6 - C_{10} alkylphenol ethoxylates. C_{14} - C_{18} linear primary alcohols condensed with from seven to thirty moles of ethylene oxide per mole of alcohol are preferred, examples being C_{14} - C_{15} (EO)₇, C_{16} - C_{18} (EO)₂₅ and especially C_{16} - C_{18} (EO)₁₁.

Suitable zwitterionic surfactants include the C_{12} - C_{16} alkyl betaines and sultaines. These and other zwitterionic and nonionic surfactants are disclosed in Laughlin & Heuring USP 3,929,678.

Bleaching agents useful in the compositions of the invention include sodium perborate, sodium percarbonate and other perhydrates at levels of from 5% to 35% by weight of the composition. Organic peroxy bleach precursors such as tetra acetyl ethylene diamine and tetra acetyl glycoluril can also be included and these and other precursors are disclosed in Belgian Patent No. 859461 published April 6th, 1978.

In compositions incorporating oxygen bleaches, bleach stabilisers are also preferred components usually at levels of from 0.2% to 2% by weight of the composition. The stabilisers may be organic in nature such as the previously mentioned amino polyacetates and amino polyphosphonates or may be inorganic such as magnesium silicate. In the latter case the material may be added to the formulation or formed in situ by the addition of a water-soluble magnesium salt to a slurried detergent mix containing an alkali metal silicate.

Suds controlling agents are often present. These include suds boosting or suds stabilising agents such as mono- or di-ethanolamides of fatty acids. More often in modern detergent compositions, suds suppressing agents are required. Soaps especially those having >18 carbon atoms, or the corresponding fatty acids, can act as effective suds suppressors if included in the anionic surfactant component of the present compositions. Usually 1% to 4% of such soap is effective as a suds suppressor. Very suitable soaps when suds suppression is a primary reason for their use, are those derived from C_{18} - C_{22} hardened marine oil fatty acids.

However, non-soap suds suppressors are preferred in synthetic detergent based compositions of the invention since soap or fatty acid tends to give rise to a characteristic odour in these compositions.

Preferred suds suppressors comprise silicones. In particular these may be employed a particulate suds suppressor comprising silicone and silanated silica releasably enclosed in water soluble or dispersible substantially non-surface active detergent impermeable carrier. Suds suppressing agent of this sort are disclosed in British patent specification 1,407,997. A very suitable granular (prilled) suds suppressing product comprises 7% silica/silicone (15% by weight silanated silica, 85% silicone, obtained from Messrs. Down Corning), 65% sodium tripolyphosphate, 25% tallow alcohol condensed with 25 molar proportions of ethylene oxide, and 3% moisture. The amount of silica/silicone suds suppressor employed depends upon the degree of suds suppression desired but it is often in the range from 0.01% to 0.5% by weight of the detergent composition. Other suds suppressors which may be used are water insoluble, preferably microcrystalline, waxes having melting point in the range from 35 to 125°C and saponification value less than 100, as described in British patent specification 1,492,938.

Yet other suitable suds suppressing systems are mixtures of hydrocarbon oil, a hydrocarbon wax and hydrophobic silica as described in European patent application Publication No. 0000216 and, especially particulate suds suppressing compositions comprising such mixtures, combined with a nonionic ethoxylate having hydrophilic lipophilic balance in the range from 14-19 and a compatibilising agent capable of forming inclusion compounds, such as urea. These particulate suds suppressing compositions are described in European patent application Publication No. 0008830.

Soil suspending agents are usually present at 0.1 to 10%, such as water soluble salts of carboxymethyl cellulose carboxyhydroxymethyl cellulose, polyethylene glycols of molecular weight from 400 to 10000 and copolymers of methylvinylether and maleic anhydride or acid.

Proteolytic, amylolytic or lipolytic enzymes, especially proteolytic, and optional brighteners, of anionic, cationic or nonionic types, especially the derivatives of sulphonated triazinyl diamino stilbene may be present. A further useful additive is a photo-activated bleach comprising mixture of the tri- and tetra sulphonated derivatives of zinc phthalocyanine as described in B. P. Specification Nos. 1372035 and 1408144.

Colours, non-substantive, and perfumes, as required to improve the aesthetic acceptability of the product, are usually incorporated.

Throughout the description herein where sodium salts have been referred to potassium, lithium or ammonium or amine salts may be used instead if their extra cost, are justified for special reasons.

Preparation of the compositions

The granular detergent compositions may be prepared by mixing the components or by co-agglomerating them but preferably they are prepared by spray drying an aqueous slurry of the non-heat-sensitive components, (a), (b) and the builder salt (c) to form spray dried granules into which may be admixed the heat sensitive components such as persalts, enzymes, and perfumes. The water soluble cationic (e) may be included in the slurry for spray drying, or it may be incorporated by dissolving or dispersing the cationic component in water or another suitable volatile liquid and then spraying this solution or dispersion onto the spray dried granules before or after other heat sensitive solids have been dry mixed with them. Alternatively the cationic component (e) can be dry mixed together with the other heat sensitive solids. The clay component may be added to the slurry for spray drying or may be dry mixed, as preferred for reasons unrelated to its softening effect, such as for optimum colour of the product.

The invention is illustrated by the following non-limiting examples.

Example 1

The following compositions were made up

		A	B
	i) Sodium linear C ₁₂ alkyl benzene sulphonate	7.5	7.5
5	i) Sodium tripolyphosphate	30.0	30.0
	i) Sodium Silicate (SiO ₂ Na ₂ O ratio 1.6:1)	5.0	5.5
10	iii) Sodium Perborate tetrahydrate	24.0	24.0
	iii) Mineral oil-hydrophobic silica-wax suds suppressor	0.2	0.2
	i) Sodium sulphate	14.0	12.0
15	ii) C ₁₂ —C ₁₄ alkyl trimethyl ammonium bromide	—	2.0
	i) Sodium Montmorillonite clay	10.0	10.0
20	i) Optical brightener	0.2	0.2
	iii) Proteolytic Enzyme	0.3	0.3
	i) Moisture and miscellaneous	8.3	8.3

25 The compositions were made by first forming designated ingredients (i) into spray dried base granules. A concentrated aqueous solution of the quaternary ammonium compound (ii) was then made up and sprayed on to the base powder to give crisp free flowing granules into which were dry mixed the remaining ingredients (iii).

30 The compositions were then used to wash 3.63 kg soiled fabric loads in a Miele Model 422 Drum Automatic machine set to a prewash-mainwash cycle in which the mainwash was a boil wash. The water hardness was 14° Clark (Ca:Mg molar ratio 2:1) and the product usage was 70 g in the prewash and 140 g in the mainwash. Artificially soiled cotton tracers and clean terry towelling tracers were added to each wash to permit evaluation of respectively, the cleaning and softening performance of the compositions. Following the wash each load was air dried at ambient temperatures before being assessed by an expert panel. No differences in cleaning performance were apparent between either of the formulations but the softness assessment was as follows.

35 In a paired comparison between terry towelling tracers washed in compositions A and B using a Scheffe scale of assessment, composition B was rated better for softness than A by 1.62 panel score units with a least significant difference (LSD) of 0.39 psu at the 95% confidence level. A comparison of the soiled swatches washed by each composition showed a slight advantage for composition B in soil removal, there being equivalent between the compositions on other soil stains.

40 It can thus be seen that composition B in accordance with the invention is superior in fabric softening performance to the prior art composition A whilst being equivalent to or slightly better than Composition A in cleaning performance.

45 In this example the C₁₄ alkyl trimethyl quaternary component may be replaced by lauryl methyl dihydroxyethyl ammonium bromide and coconut alkyl trimethyl ammonium bromide whilst the sodium montmorillonite may be replaced by calcium montmorillonite, sodium hectorite or sodium saponite.

Example 2

The following composition is in accordance with the invention

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		2
	Sodium C ₁₂ linear alkyl benzene sulphonate	8.0
5	C ₁₂ -C ₁₄ alkyl trimethyl ammonium chloride	3.0
	Sodium montmorillonite clay	10.0
10	Sodium Sulphate	12.0
	Sodium tripolyphosphate	45.0
15	Sodium Silicate (SiO ₂ Na ₂ O ratio =1.6:1)	10.0
	Silica-Silicone suds suppressor	0.2
20	Tetra sodium ethylene diamine tetra methylene phosphonate	0.2
	Stearic Acid	0.2
25	Tetrasulphonated zinc phtalocyanine	0.2
	Optical Brightener	0.1
	Proteolytic Enzyme	0.3
30	Perfume	0.2
	Moisture and Miscellaneous	10.6
35		

Claims

1. A granular detergent composition comprising, by weight of the composition,
- 40 (a) 5-10% of an anionic surfactant from water soluble salts of alkyl benzene sulfonates, alkyl sulfates, paraffin sulfonates, alpha olefin sulfonates, soaps;
- (b) from 2% to 12% of an impalpable smectite-type clay mineral of particle size less than 50 μ m having an ion exchange capacity of at least 50 meq per 100g selected from sodium and calcium montmorillonite, sodium hectorite and sodium saponite;
- 45 (c) from 10% to 80% of a detergent builder salt; and
- (d) optionally other laundry detergent components characterised in that the composition also comprises;
- (e) 1-3% of a water soluble nitrogenous cationic organic compound selected from quaternary ammonium compounds of formula $R_7R_8R_9R_{10}N^+X^-$ wherein R_7 is C₈-C₁₄ alkyl, each of R_8 R_9 and R_{10} is independently C₁-C₄ alkyl or hydroxyethyl and X is an anion, said cationic compound being present as a solid component
- 50 dry mixed with spray dried granular components of said composition or as a spray-on of a solution or dispersion to the surface of, or as part of spray dried granules comprising components (a) (c) and optionally (b) and/or (d);

provided that the molar ratio of component (e) to (a) is less than 1:1; the amounts of (a), (b), (c), (e), and, if present, (d) comprising a total of 100%, the optional components (d) being comprised by nonionic and zwitterionic surfactants, bleaching agents and organic precursors therefor, and suppression agents, said suspending and anti redeposition agents, enzymes optical brighteners, colouring agents and perfumes.

2. A detergent composition according to claim 1 wherein the molar ratio of (e) to (a) is less than 1:2

3. A detergent composition according to either one of claims 1 and 2 wherein the water soluble cationic

compound (e) is selected from quaternary ammonium salts in which R_7 is C_{12} - C_{14} alkyl and R_8 , R_9 , R_{10} are selected from methyl and hydroxyethyl groups.

5 Patentansprüche

1. Eine granulare Waschmittelzusammensetzung, enthaltend in Gew.-% bezogen auf die Zusammensetzung:

- (a) 5-10 % eines anionischen oberflächenaktiven Mittels, ausgewählt aus wasserlöslichen Salzen von Alkylbenzolsulfonaten, Alkylsulfaten, Paraffinsulfonaten, alpha-Olefinsulfonaten, Seifen;
- (b) 2 bis 12 % eines sehr feinen nicht tastbaren Smectit-artigen Tonminerals einer Teilchengröße von weniger als 50 μm mit einer Ionenaustauschkapazität von wenigstens 50 mÄq je 100 g, ausgewählt aus Natrium- und Calcium-Montmorillonit, Natriumhectorit und Natriumsaponit;
- (c) 10 bis 80 % eines Detergens-Gerüststoffsalzes; und
- (d) wahlweise andere Waschmittelkomponenten, dadurch gekennzeichnet, daß die Zusammensetzung weiterhin umfaßt:
- (e) 1-3 % einer wasserlöslichen stickstoffhaltigen kationischen organischen Verbindung, ausgewählt aus quaternären Ammoniumverbindungen der Formel



worin R_7 C_8 - C_{14} -Alkyl bedeutet, jede Gruppe R_8 , R_9 , R_{10} unabhängig voneinander C_1 - C_4 Alkyl oder Hydroxyethyl bedeutet und X ein Anion ist, wobei die kationische Verbindung vorhanden ist als feste Komponente, die trocken zusammengemischt ist mit den Sprühgetrockneten Granulatkomponenten der Zusammensetzung, oder als eine Aufsprühung auf die Oberfläche einer Lösung oder einer Dispersion oder als ein Teil sprühgetrockneter Granulate, umfassend die Komponenten (a), (c) und wahlweise (b) und/oder (d),

vorausgesetzt, daß das molare Verhältnis der Komponente (e) zu (a) weniger als 1:1 beträgt und die Mengen an (a), (b), (c), (e) und, falls vorhanden (d) eine Gesamtmenge von 100% ergeben, und die wahlweisen Komponenten (d) nicht nicht-ionische und zwitterionische oberflächenaktive Mittel, Bleichmittel und organische Vorläufer hierfür, Schaumsuppressoren, Schmutz-Suspensionsmittel und Schmutz-Ablagerungsinhibitoren, Enzyme, optische Aufheller, Farbstoffe und Parfüme umfassen.

2. Eine Waschmittel-Zusammensetzung gemäß Anspruch 1, worin das molare Verhältnis von (e) zu (a) weniger als 1:2 beträgt.

3. Eine Waschmittel-Zusammensetzung gemäß einem der Ansprüche 1 oder 2, worin die wasserlösliche kationische Verbindung (e) ausgewählt ist aus quaternären Ammoniumsalzen, worin R_7 C_{12} - C_{14} -Alkyl bedeutet und R_8 , R_9 und R_{10} ausgewählt sind aus Methyl- und Hydroxyethylgruppen.

Revendications

- 1. Une composition détergente granulaire contenant, en poids de la composition,
 - a) 5-10% d'un agent de surface anionique choisi parmi les sels hydrosolubles d'alkylbenzènesulfonates, d'alkylsulfates, de paraffinesulfonates, d'alpha-oléfinesulfonates, les savons ;
 - b) de 2 à 12% d'une argile impalpable de type smectite d'une granulométrie inférieure à 50 μm possédant une capacité d'échange d'ions d'au moins 50 méq. pour 100 g, choisie parmi les montmorillonites de sodium et de calcium, l'hectorite de sodium et la saponite de sodium ;
 - c) de 10% à 80% d'un sel auxiliaire de détergence et,
 - d) facultativement d'autres constituants détergents pour blanchissage, caractérisée en ce que la composition renferme également
 - e) 1-3% d'un composé organique azoté cationique hydrosoluble choisi parmi des composés d'ammonium quaternaire de formule $R_7R_8R_9R_{10}N^+X^-$ dans laquelle R_7 est un alkyle en C_8 - C_{14} , chacun des R_8 , R_9 et R_{10} est, indépendamment, un alkyle ou un hydroxyalkyle en C_1 - C_4 et X est un anion, ledit composé cationique étant présent en tant que constituant solide mélangé à sec avec des constituants granulaires de ladite composition séchés par atomisation, sous forme de pulvérisation d'une solution ou d'une dispersion sur la surface de granulés séchés par atomisation ou en tant que partie de granulés séchés par atomisation contenant les constituants a), c) et facultativement b) et/ou d), sous réserve que le rapport molaire du constituant e) à a) soit inférieur à 1:1 ; les quantités de a), b), c), e) et, le cas échéant de d) représentant un total de 100%, les constituants facultatifs d) comprenant des agents de surface non ioniques et zwitterio-

riques, des agents deblanchiment et leurs précurseurs organiques, des supprimeurs de mousse, des agents de mise en suspension de salissures et d'antiredéposition, des enzymes, des azurants optiques, des colorants et des parfums.

2. Une composition détergente selon la revendication 1, dans laquelle le rapport molaire de e) à a) est inférieur à 1:2

3. Une composition détergente selon l'une ou l'autre des revendications 1 et 2, dans laquelle le composé cationique hydrosoluble e) est choisi parmi les sels d'ammonium quaternaire dans lesquels R_7 est un alkyle en C_{12} - C_{14} et R_8 , R_9 et R_{10} sont choisis parmi les groupes méthyle et hydroxyméthyle.

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